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Assessment of CO_2 bubble generation influence on direct methanol fuel cell performance

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Abstract

Fuel cells fed directly by liquid methanol represent a class of suitable devices for supply portable small power applications. To become a market attractive technology some issues must be properly addressed and resolved. The presence of gaseous CO_2 generated in the anode channels is the main issue as it can hinder the free surface of the Gas Diffusion Layer reducing the active area and the methanol flux through the porous media towards the catalyst layer. In this work the influence of gas phase fraction on the cell performance and the relationship with the operating parameters such as air flow rate, methanol-water solution flow rate and current density is investigated. The characterization of CO_2 bubbles flow in the anode channel is carried out.

Peer-review under responsibility of Applied Energy Innovation Institute

Keywords: DMFC, methanol, CO_2 bubbles, fuel cell

1. Introduction

Fuel cells are a good solution for the battery replacement in those systems where a high quantity of energy have to be stored [1]. Coupling electrolytic cells and fuel cells with a renewable sources plant is demonstrated to be an attractive alternative for saving energy surplus generated by aleatory energy sources such as solar and wind [2]. In recent years research focused its efforts to increase lifecycle, reliability and to reduce costs of the fuel cell technology [3]. The aim of this work is to characterize the CO_2 bubbles generation and transport mechanism in the anode of the cell and their influence on the Direct Methanol Fuel Cells (DMFCs) performance [4]. The presence of gaseous CO_2, as product of the methanol oxidation in the Anode Catalyst Layer (ACL), can lead to the hindering of the free surface of the Gas Diffusion Layer (GDL), thus reducing the useful active area and the methanol mass transport in the porous media.

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Nomenclature

A_w wetted area (m^2)
C methanol concentration (mol m^{-3})
D diffusion coefficient (m^2 s^{-1})
F Faraday number
J_{met} methanol mass flux (kg $m^{-2}s^{-1}$)
PM molecular weight
S generation rate (kg s^{-1})
V volume (m^3)
V_m gas molar volume (m^3 mol)
δ water drag coefficient
e air excess
h channel height (m)
i current density (mA cm^{-2})
m mass flow rate (kg s^{-1})
s stoichiometric coefficient
t_m membrane thickness (m)
t_r residence time (s)
x_{met} methanol molar fraction
z moles of electrons

2. Material and Methods

The experimental campaign was conducted using a specifically developed fuel cell designed and built in our laboratory (Fig. 1). The support structure was made in plexiglass, the current collectors were made with Stainless Steel 316 (SS316) and they were machined in our laboratories of DIMA (Dipartimento di Ingegneria Meccanica e Aerospaziale). They consists in SS316 plates with a serpentine channels with width 2 mm, depth 2.7 mm, and length 20 mm separated by ribs with width 1 mm (Fig. 2a). PTFE sealing gaskets were used to insulate current collectors from the electrolyte and to prevent short circuit and liquid leakage. The Membrane Electrode Assembly (MEA) is a Nafion 117 membrane with PtRu 1:1 catalysts loading of 4 mg/cm^2 at the anode and only Pt at the cathode. Gas Diffusion Layer (GDL) is made of carbon cloth.

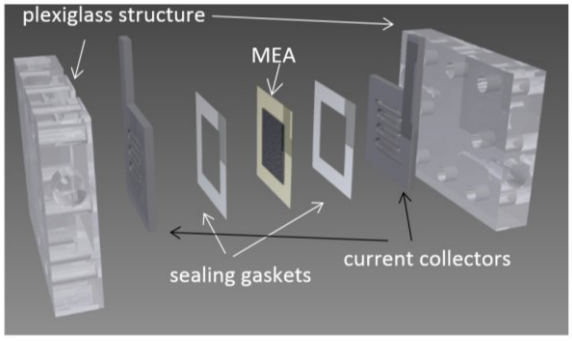


Fig. 1. Sketch of fuel cell assembly

Passive DMFCs have only two influence parameters to be assessed (OR and geometry). This made simpler the development of an advanced configuration on the basis of the optimization of the two parameters. The geometry of the serpentine (Fig. 2a) and its Open Ratio (OR) [5] were assessed in the previous studies focused on the passive DMFCs [6,7].

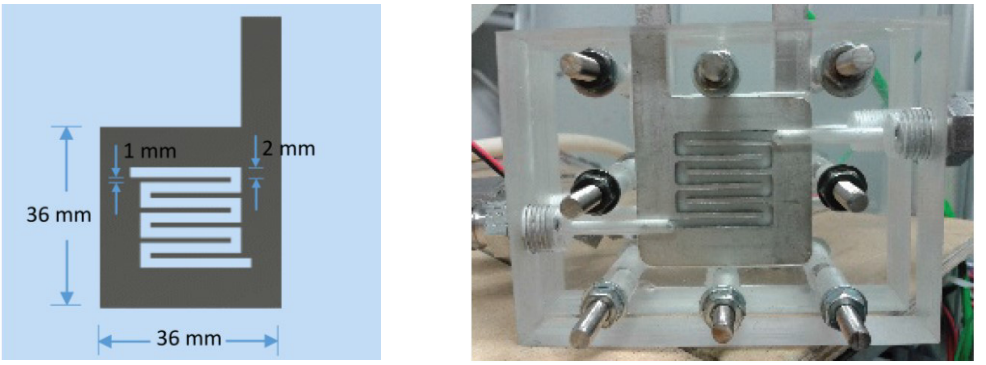


Fig. 2. a) Current collector draw; b) Fuel cell assembly

2.1. Data acquisition for VI and power curves was made with a Bio-Logic® SP-150 Potentiostat. The MEA was activated at 0.3 V for 24h then, the used procedure was based on the DURAMET protocol by CNR [8]. The DURAMET procedure is specified in the following

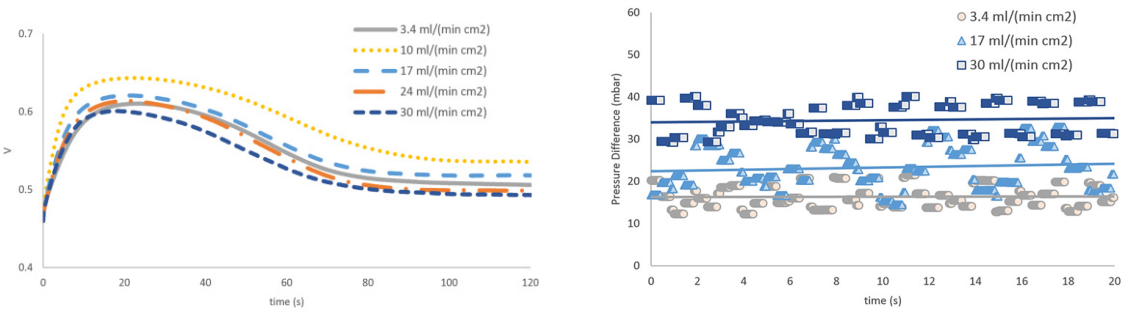
1. Costant Current Method : 7 min @ 350 mA;
2. Open Circuit Voltage : 2 min @ OCV ;
3. V-I Curve : from 0,450 V to 0,150 V @ of 1 mV/s ;
4. V-I Curve : from 0,150 V to 0,460 V @ of 1 mV/s ;
5. Open Circuit Voltage : 2 min @ OCV ;
6. Costant Current Method : 7 min @ 350 mA;

3. Results and discussion

Open Circuit Voltage (OCV) tests show different voltage behavior, depending on: a) methanol flow rate due to the diffusion of the fuel into the GDL and b) the permeability of the membrane that causes fuel cross-over. Tests shows that the dependence between fuel flow rate and OCV is not linear. OCV reaches a stable situation after 120 s of recording. The cross-over phenomena depends on gradient concentration between the anode and the cathode, as shown by the (1).

$$J_{met} = D_{met}\frac{(C_{met,a} - C_{met,c})}{t_m} + \frac{C_{met,a}k\Delta p}{t_m \mu} + x_{met,a}\delta\frac{i}{F} \qquad (1)$$

In OCV tests the methanol concentration is kept constant, current density is null while the anode-cathode differential pressure increases as the water-methanol flow rate increases. As can be seen in Fig. 3a, the OCV increases as the flow rate decreases up to 10 ml min^{-1} cm^{-2} whereas for 3.4 ml min^{-1} cm^{-2} the OCV results to be lower. In this measurement the mean differential pressure between anode and cathode (Fig. 3b), and then the linearity of the cross-over phenomena with the increase of the pressure difference, shows that OCV is influenced by further phenomena acting on the concentration gradient.



a) b)

Fig. 3. a) OCV test at different methanol-water flow rates; b) Measurements of differential pressure between anode and cathode

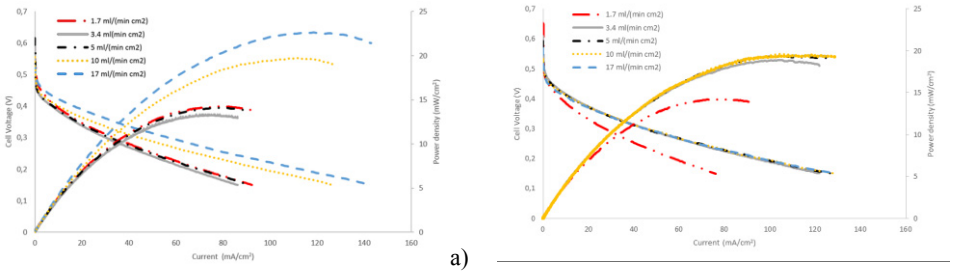
3.1. Air flow rate investigation

The decrease in OCV also depends on the air flow rate delivered at the cathode. As the differential pressure between anode and cathode changes, also the pressure force that drives methanol from anode to the cathode changes, see (1) [9]. The influence of the cathode flow rate was also investigated. Assuming as reference the stoichiometric air needed to produce 60 mA cm^{-2}, two excess flow rates (2) were considered (see Table 1). Changes in polarization curves for different fuel flow rates in the two cases are shown in Fig. 4.

$$e = \frac{m_{exp}}{m_{st}} = \frac{m_{exp}}{s_{ox} P M_{ox} I / 0.21 z F} \qquad (2)$$

Table 1. Air flow excess at $i = 60\ mA\ cm^{-2}$

e	5	40
air flow rate (ml min^{-1} cm^{-2})	*6*	*50*



a) b)

Fig. 4. Polarization curves with air flow rate respectively a) 6 ml min^{-1} cm^{-2} and b) 50 ml min^{-1} cm^{-2}

The increase in air flow rates compensates the effect of differential pressure between anode and cathode. The term of the methanol cross-over, related to the differential pressure decreases for all the water-methanol flow rate when the air excess increases. As can be seen from Fig. 4a at lower e (e=5) the polarization and power curves increases when the flow rate increase. In the Fig. 4b all the polarization curves have the same behaviour except for the 3.4 ml min^{-1} cm^{-1} flow rate that shows a higher concentration losses for higher current density.

3.2. Fuel flow rate investigation

The behaviour noted when discussing Fig. 4b is confirmed with a higher value of air flow rate (150 ml $min^{-1}cm^{-2}$) in a wider range of methanol flow rate, from 3.4 up to 30 ml $min^{-1}cm^{-2}$ (Fig. 5).

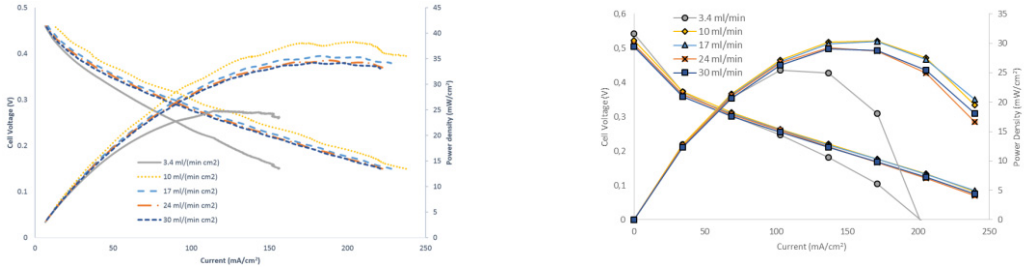


Fig. 5. Polarization curves changing methanol flow rate obtained by a) voltage steps of 1 mV s^{-1}; b) current steps

Again at 3.4 ml min^{-1} cm^{-2} very strong losses are present. To investigate the influence of the bubbles on the cell performance the characteristic curve measured with DURAMET protocol was replaced with constant current steps of 2 minutes each. This means we argue that such losses can be attributed to CO_2 bubbles generation. Keeping constant the gas generation rate in the anode channel, as can be seen from the relationship between current density and CO_2 flow in (3).

$$S_i = \frac{s_i \cdot i \cdot PM_i}{z \cdot F} \tag{3}$$

The characteristics measured with the two procedures (shown in Fig. 5) have the same behaviour. For higher anode flow rates the power density has roughly the same values. For 3.4 ml min^{-1} cm^{-2} the cell performance is lower. Over a certain value of anode flow rate, other phenomena influence the cell performance. It is arguable that this depends on the CO_2 bubbles generation. For bubbles characterization, a statistical investigation was made by analysing the images carried out by a PIV analysis.

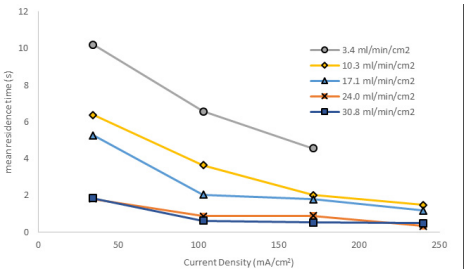


Fig. 6. Mean residence time of the bubbles in the anode channels

As can be seen in Fig. 6, the lower flow rates are affected by the higher residence time of the bubbles. For 3.4 ml min^{-1} cm^{-2}, the methanol flow rate has been affected by a mean time residence that is almost twice with respect to the other flow rates. Recent PIV measurements at the lower flow rate showed that the lower flow rate favoured the coalescence between CO_2 bubbles, allowing the generation of a slug flow in the channel, eventually temporary blocking the flow of fresh fuel towards the ACL (see Fig. 7). The power drop, at lower flow rates, has to be attributed to the CO_2 bubbles coalescence that globally reduces the cell power density by a 40 %, at higher current densities.

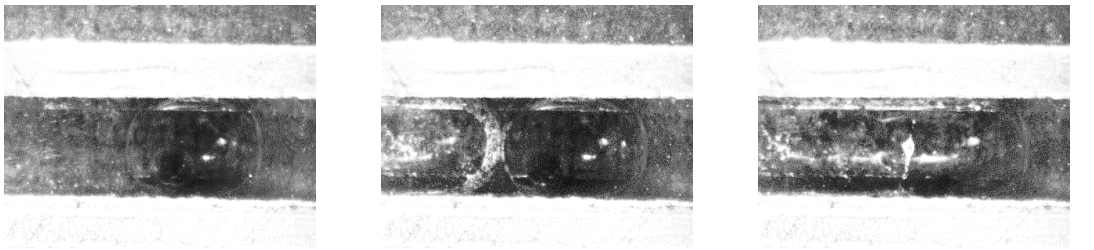


Fig. 7. Bubbles coalesce generating a plug flow

This is in agreement with the numerical findings of Kulikovsky [9] who carried out a mathematical model and concluded that under moderate methanol stoichiometries the bubbles reduce limiting current of the cell by a factor of 3-4.

4. Conclusions

The effects of the CO_2 bubbles in the anode channel of the DMFC were investigated. VI and Power test showed the improvement of the cell performance with higher flow rates. The bubbles shows a decrease in mean diameter when the flow rate increases. Smaller are the bubbles easier is the detachment from GDL and the removal under the thrust of the liquid phase. As the residence time of the bubbles at lower flow rate is higher, bubbles grow thus hindering methanol passage through GDL pores. For flow rate 3.4 ml $min^{-1}cm^{-2}$, bubble diameter is comparable with the channel width and the bubbles detach from the GDL under the thrust of methanol flux. For higher flow rate the strength of the flow is higher then the bubble size for detachment is smaller. The removal is then more efficient. The coalescence of bubbles can cause a decrease in generated power in particular when the flow rate is small and the current density is high. For anode flow rate 3.4 ml min^{-1} cm^{-2}, we noticed that bubbles generation reduces the power also more than 40 %.

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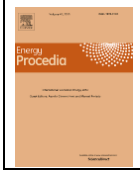

Biography

My name is Andrea Calabriso and I am a PhD student at ‘Sapienza - University of Rome’. My research is focused on experimental and numerical studies about DMFCs. The main part of my PhD thesis is concentrated on the micro-PIV analysis of the two-phase flow in the fuel cell micro-channels.